I.
INTEGRATED INTENSITY MEASUREMENTS FOR VIBRATION-ROTATION BANDS OF CARBON DIOXIDE

II.
TOTAL ABSORPTIVITY MEASUREMENTS ON CARBON DIOXIDE AT ROOM TEMPERATURE

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ABSTRACT

I. This study contains an outline of the experimental measurements performed in order to determine integrated intensities of various vibration-rotation bands of carbon dioxide by use of standard techniques with a Perkin-Elmer spectrometer.

II. Total absorptivity measurements on carbon dioxide at room temperatures were made in a pressurized gas cell provided with transparent windows.

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SYMBOLS

Part I

| | | |
|---|---|---|
| $\alpha$ | = | integrated intensity |
| $P_\omega$ | = | spectral absorption coefficient |
| $\omega$ | = | wave number |
| v | = | quantum number |
| $I_\omega$ | = | transmitted intensity |
| $I_{o\omega}$ | = | incident intensity |
| p | = | partial pressure |
| $\ell$ | = | optical path length |
| $T_{o\omega}$ | = | apparent intensity without absorber |
| $T_\omega$ | = | apparent intensity with absorber |
| $\alpha'$ | = | apparent integrated intensity |
| $\beta$ | = | $p\ell/\alpha'$ |
| $p_T$ | = | total pressure |
| T | = | micrometer screw turns |
| B | = | defined spectrometer constant |
| $\omega_2$ | = | Restrahlen wave number |
| $p\ell$ | = | optical density |

Part II

| | | |
|---|---|---|
| $R_\lambda$ | = | energy emitted by a blackbody at temperature T at wave length $\lambda$ |
| $R_\omega$ | = | energy emitted by a blackbody at temperature T at wave number $\omega$ |

SYMBOLS (Cont'd)

| | | |
|---|---|---|
| $\lambda$ | = | wave length |
| $\omega$ | = | wave number |
| $c_1, c_2$ | = | physical constants |
| c | = | velocity of light |
| h | = | Planck's constant |
| k | = | Boltzmann's constant |
| T | = | absolute temperature |
| $\sigma$ | = | Stephan Boltzmann constant |
| $\varepsilon$ | = | emissivity |
| $R_\omega$ | = | spectral intensity of emission from greybody |
| E | = | engineering emissivity |
| K | = | recorder constant |
| K' | = | defined recorder constant |
| D | = | recorder deflection |
| $\alpha$ | = | absorptivity |
| $T_s$ | = | globar temperature |

# I. INTEGRATED INTENSITY MEASUREMENTS ON CARBON DIOXIDE

## A. Introduction and Summary

The importance of gas radiation in effecting heat transfer between a gas and its surroundings, particularly when the gas temperature is high, has been recognized for some time. However, accurate emissivity data are generally not available for use in engineering calculations of heat transfer. Recently attempts have been made to calculate gas emissivities theoretically from spectroscopic data. It is the purpose of the present study to provide some of the basic data which are needed for the theoretical calculation of emissivities of carbon dioxide.

Quantitative infrared intensity measurements have been carried out for the more intense vibration-rotation bands of carbon dioxide using helium as a pressurizing agent. Measurements were made by use of standard techniques. The results are summarized in Table I.

Table I. Observed Integrated Intensities* of Carbon Dioxide

| Band Center ($cm^{-1}$) | Integrated Intensity ($cm^{-2}$ $atm^{-1}$ at 298°K) | Band Center ($cm^{-1}$) | Integrated Intensity ($cm^{-2}$ $atm^{-1}$ at 298°K) |
|---|---|---|---|
| 5109 | .43 | 1932, 1886 combined | .83 |
| 4983 | 1.01 | | |
| 4860 | .27 | 720, 668, 647, 618 combined | 171.50 |
| 3716 | 42.30 | | |
| 3609 | 28.50 | | |
| 2349 | 2706.00 | | |
| 2137, 2094, 2074 combined | .147 | | |

* Observed intensities are accurate within ± 20%.

B. Methods For the Experimental Determination of Integrated Intensities

Integrated intensities of the infrared vibration-rotation bands are required for the theoretical calculation of gas emissivities and radiant heat transfer.

The integrated intensity $\alpha$ for a given vibration-rotation band is defined by the relation

$$\alpha = \int P_\omega \, d\omega \qquad (1)$$

where $P_\omega$ represents the spectral absorption coefficient at the wave number $\omega$. Although the limits of integration should extend from $-\infty$ to $+\infty$ it is sufficient to restrict integration to a narrow wave number interval bracketing the band center because $P_\omega$ decreases very rapidly with $\omega$ in the wings of the vibration-rotation bands. The integrated intensities for various vibration-rotation bands will be identified by appropriate changes in vibrational quantum number. For example, the intense $\nu_3$ - fundamental of carbon dioxide arises as a result of the transition* (2)

$$v_1 = 0 \rightarrow v_1 = 0, \quad v_2 = 0 \rightarrow v_2 = 0, \quad l = 0 \rightarrow l = 0, \quad v_3 = 0 \rightarrow v_3 = 1$$

and has a band center at 2349.3 $cm^{-1}$. The corresponding value of the integrated intensity is then identified by the symbol

---

* For details concerning spectroscopic notation of polyatomic molecules see, for example, G. Herzberg, Infrared and Raman Spectra, D. Van Nostrand Co., New York (1945).

$$\alpha \ (0,0,^{0}_{0} \rightarrow 0,0,^{0}_{1})$$

The integrated intensities of other vibration-rotation bands may be identified similarly.

a) The Method of Wilson and Wells[2]

For monochromatic radiation it is well known that

$$I_\omega = I_{0\omega} \exp(-P_\omega \ p\ell) \qquad (2)$$

where $I_\omega$ is the transmitted intensity at the wave number $\omega$ when the incident intensity is $I_{0\omega}$, p is the partial pressure of the absorbing gas and $\ell$ represents the optical path length. Hence the integrated intensity becomes

$$\alpha = (p\ell)^{-1} \int_{\Delta\omega} \ln (I_{0\omega} / I_\omega)\, d\omega \qquad (3)$$

where the integration in Eq. (3) is to be performed over the entire effective width $\Delta\omega$ of the vibration-rotation band under study.

The apparent intensities observed without absorber and with absorber, when the instrument is set at $\omega$, are not $I_{0\omega}$ and $I_\omega$ respectively, but rather

$$T_{0\omega} = \int I_{0\omega'} \ g(\omega, \omega')\, d\omega' \qquad (4)$$

and

$$T_\omega = \int I_{\omega'} \ g(\omega, \omega')\, d\omega' \qquad (5)$$

where $g(\omega, \omega')$ represents the fraction of light of actual wave number $\omega'$ to which the instrument responds when it is set at $\omega$. Some of the difficulties inherent in the calculation of $P_\omega$ do not arise in the determination of the integrated intensity. From experimentally determined values of $T_\omega$ and $T_{0\omega}$ it is possible to determine an apparent integrated intensity $\alpha'$ which is defined by the relation

$$\alpha' = (p\ell)^{-1} \int \ell n \, (T_{0\omega} / T_\omega) \, d\omega = \beta / p\ell \qquad (6)$$

Wilson and Wells[2] have shown that

$$\lim_{p\ell \to 0} \alpha' = \alpha$$

when a number of specified conditions are met. These conditions include the requirement that $I_{0\omega}$ be independent of $\omega$ in the resolved spectral range, a condition which can be approached closely by eliminating atmospheric absorption and using sufficiently narrow spectrometer slits to give high spectral resolution. In addition to requiring constant $T_{0\omega}$, Eq. (6) will hold only if either the variation of $P_\omega$ with $\omega$ can be neglected in the spectral range or the resolution of the instrument does not vary appreciably over the vibration-rotation band under study. Of these two requirements the latter constitutes an intrinsic property of the instrument. The variation of $P_\omega$ in the resolved spectral interval can be minimized

by pressure broadening, i.e., as $p\ell$ is decreased, $\alpha'$ will approach $\alpha$ more rapidly, the higher the constant total pressure at which the observations are made.

As the optical density is decreased, the plot of $\beta$ vs $p\ell$ may show considerable curvature. This fact introduces an appreciable error into the extrapolation required to determine $\alpha$. At sufficiently high total pressure $p_T$, the variation of $\beta$ with $p\ell$ should follow a linear relation in accord with the fact that the true integrated intensity is measured at every value of the optical density and Eq. (6) should apply directly. By proceeding according to Wilson and Wells[2] the result $\alpha' \rightarrow \alpha$ as $p_T$ is increased can be demonstrated.[3]

The true value of the integrated intensity $\alpha$ can be obtained either by extrapolating $\alpha'$ to zero values of $p\ell$ at constant $p_T$ or by finding the limiting value of $\alpha'$ at constant optical density as the total pressure is increased.

b) The Self-Broadening Technique of Penner and Weber[4]

Infrared transmission studies on pure gases have the obvious advantage of eliminating the possibility of experimental error resulting from imperfect mixing or from the occurrence of adsorption-desorption phenomena. On the other hand, they possess the severe disadvantage of always involving the effect of significant self-broadening associated with increased pressure of the absorber. How-

ever, by suitable choice of test cell length it is possible to utilize self-broadening to obtain quantitative infrared intensity data. In general, the required cell length is shorter when the vibration-rotation band is more intense.

C. Experimental Studies

a) Apparatus

A Perkin-Elmer Model 12C single beam infrared spectrometer with lithium fluoride, sodium chloride, and potassium bromide prisms was used for transmission measurements. Incorporation of automatic slit drive over the wavelength interval used for study was found to save considerable time in experimental work. Pressure readings were performed by use of a Wallace and Tiernan precision manometer for the pressure range 0-800 mm of mercury ( ± .2 mm) and 0-1000 psig by use of a Marsh gage ( ± 2 psig).

The cell and window assemblies were machined from 18-8 stainless steel stock. Neoprene O-rings and neoprene or teflon gaskets were used to support the cell windows. The principal features of the cell are shown in Fig. 1. The right end plate is provided with a special tap to permit flushing with nitrogen of the outside of the cell in the light path. This same end plate is fitted with a flange to slide into the absorption cell slot provided on the spectrometer. A flexible collar is inserted between the other end plate and the globar source. The collar also has a fitting for nitrogen flushing.

The cell is provided with a window assembly as shown and is large enough to permit incorporation of stirring rod with perforated end plate. In each experiment care was taken to assure uniform mixing of gases in the cell by adequate use of the stirrer. It was assumed that a uniform gas mixture had been obtained when additional stirring produced no measurable change in transmission.

Details of wavelength calibration of the prism spectrometer using a sodium chloride prism are given in Section E.

b) Summary of Experimental Data

For the vibration-rotation bands of carbon dioxide on which experimental measurements were performed the quantity $\beta/2.303$ has been plotted as a function of $p\ell$ in Figs. 2 to 10. Corresponding integrated intensities have been given previously in Table I.

## D. Comparison With The Results of Other Investigators

The observed intensities of vibration-rotation bands of carbon dioxide are compared with the results of other investigators in Table II. Reference to Table II shows that the data are in excellent agreement with the results of other investigators.

Table II. Observed Intensities of Carbon Dioxide

| Band Center ($cm^{-1}$) | Integrated Intensity $\alpha$ ($cm^2$ $atm^{-1}$ at 298°K) Wilson et al [2,5,6] (1941) | Eggers and Crawford [7] ± 10% (1951) | Present Study ± 20% (1952) |
|---|---|---|---|
| 5109 | | | .426 |
| 4983 | | | 1.01 |
| 4860 | | | .272 |
| 3716 | | 39.0 | 42.3 |
| 3614 | | 27.0 | 28.5 |
| 2349 | 2867.0 | 2693.0 | 2706.0 |
| 2137 | | | |
| 2094 | | | combined .147 |
| 2074 | | 0.14 (P and Q) | |
| 2074 | | .05 (Q only) | |
| 1932 | | .005 | combined .083 |
| 1886 | | | |
| 720 | | | |
| 668 | 187.0 | 161.0 | combined 171.5 |
| 647 | | | |
| 618 | | | |

E. Calibration of Perkin-Elmer Spectrometer with Sodium Chloride Prism

In the wave number calibration of an infrared spectrometer it may become necessary to make use of the relation between micrometer screw turns and wave number in wave number regions where no calibration points (absorption bands or lines) exist or are available.

In the present calibration it was necessary to extrapolate the micrometer screw turns vs. wave number curve from the carbon dioxide band at 667 $cm^{-1}$ to regions near the absorption limit of the sodium chloride prism. This was done using the method of McKinney and Friedel,[8] whose empirical equation is

$$T = T_o - B\,(\omega_2^{\,2} - \omega^{\,2})^{-1} \qquad (7)$$

where T is micrometer screw turns and $T_o$ is the ordinate intercept at $B(\omega_2^{\,2} - \omega^{\,2})^{-1} = 0$. Here $\omega_2$ is the Restrahlen wave number depending on the prism material and $\omega$ is a known or measured wave number. Seven absorption maxima of ammonia and carbon dioxide were used for calibration and $(\omega_2^{\,2} - \omega^{\,2})^{-1}$ was calculated and plotted against micrometer screw turns. For sodium chloride the value of $\omega_2$ is 125 $cm^{-1}$.

The constants $T_o$ and B are determined from the known absorption maxima. Equation (7) is used to extend the calibration curve of T vs $\omega$. The correction term for short wave length absorption was neglected for the present purpose. Figures 11 and 12 are reproductions

of original calibration graphs in which the abscissae are, respectively, $\omega$ and $(\omega_2^2 - \omega^2)^{-1}$, whereas each ordinate represents micrometer screw turns.

## II. TOTAL ABSORPTIVITY MEASUREMENTS ON CARBON DIOXIDE AT ROOM TEMPERATURE

### A. Introduction and Summary

The calculation of radiant heat transfer from heated carbon dioxide requires the use of experimentally determined absorptivity data. The total absorption of radiation by carbon dioxide has been reinvestigated at various optical densities at different total pressures and at room temperature. A complete investigation could not be carried out at other temperatures because of experimental difficulties with the gas cell and amplifying system. The measured values of the total absorptivities are given in Table III.

Table III. Absorptivity $\alpha$ of Carbon Dioxide at Room Temperature and Different Total Pressures ($p\ell$ refers to optical density of carbon dioxide).

| $P_T$ (atm) | $p_{co_2}/p_T$ = .012 | | $p_{co_2}/p_T$ = .0596 | | $p_{co_2}/p_T$ = .1560 | | $p_{co_2}/p_T$ = .2705 | | $p_{co_2}/p_T$ = .5177 | | $p_{co_2}/p_T$ = 1 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $p\ell$ (ft atm) | $\alpha$ | $p\ell$ (ft atm) | $\alpha$ | $p\ell$ (ft atm) | $\alpha$ | $p\ell$ (ft atm) | $\alpha$ | $p\ell$ (ft atm) | $\alpha$ | $p\ell$ (ft atm) | $\alpha$ |
| 1 | .00226 | .015 | .0112 | .024 | .0294 | .038 | .0510 | .041 | .0976 | .050 | .189 | .061 |
| 2.36 | .00534 | .023 | .0266 | .026 | .0695 | .053 | .1205 | .056 | .230 | .067 | .445 | .084 |
| 3.72 | .00841 | .027 | .0418 | .039 | .1095 | .063 | .190 | .070 | .363 | .079 | .702 | .095 |
| 5.08 | .0115 | .030 | .0571 | - | .1495 | .066 | .259 | .079 | .496 | .086 | .959 | .103 |
| 7.80 | .0176 | .035 | .0877 | .052 | .230 | .076 | .380 | .080 | .751 | .102 | 1.47 | .114 |
| 14.60 | .0318 | .043 | .164 | .062 | .430 | .086 | .745 | .094 | 1.43 | .104 | 2.76 | .133 |
| 21.41 | .0485 | .048 | .241 | .070 | .631 | .090 | 1.093 | .102 | 2.09 | .112 | 4.04 | .148 |
| 35.01 | | | | | | | | | | | 6.60 | .160 |
| 48.62 | | | | | | | | | | | 9.17 | .214 |
| 55.42 | | | | | | | | | | | 10.45 | .225 |

B. Basic Radiation Laws

The spectral distribution of radiation from a blackbody is given by Planck's radiation law[9]

$$R_\lambda \, d\lambda = c_1 \lambda^{-5} \left[\exp (c_2/\lambda T) - 1\right]^{-1} d\lambda \qquad (7)$$

where $R_\lambda \, d\lambda$ is the energy emitted from a blackbody at temperature T per unit time per unit area in the wave length interval from $\lambda$ to $\lambda$ plus $d\lambda$ throughout a solid angle $2\pi$ steradians. $c_1$ and $c_2$ are physical constants whose values are given below:[10]

$c_1 = 2\pi ch^2 = (3.732 \pm .006) \times 10^{-5}$ erg cm$^2$ sec;

$c_2 = ch/k = (1.436 \pm .001)$ cm $^\circ$K;

c = velocity of light = $(2.99776 \pm .00020) \times 10^{-10}$ cm sec$^{-1}$;

h = Planck's constant = $6.62 \times 10^{-27}$ erg sec;

k = Boltzmann's constant = $1.381 \times 10^{-16}$ ergs per molecule $^\circ$K$^{-1}$.

Equation (7) may be expressed in terms of wave number $\omega$ $(= \lambda^{-1})$,

$$R_\omega \, d\omega = c_1 \omega^3 \left[\exp (c_2 \omega/T) - 1\right]^{-1} d\omega \qquad (8)$$

where $R_\omega \, d\omega$ is the energy emitted from a blackbody at temperature T per unit time per unit area in the wave number interval from $\omega$ to $\omega$ plus $d\omega$ throughout a solid angle $2\pi$ steradians.

The total intensity of radiation emitted by a blackbody over all wave lengths is given by Stephan's law

$$\int_0^\infty R_\omega \, d\omega = \sigma T^4 \tag{9}$$

where $\sigma$ represents the Stephan-Boltzmann constant and has the numerical value[10] $(5.67283 \pm .0037) \times 10^{-5}$ erg cm$^{-2}$ $^\circ$K$^{-4}$ sec$^{-1}$ $(= 2\pi^5 k^4/15c^2h^3)$. For a greybody the emissivity $\varepsilon$ is independent of wave number, i.e.,

$$R_\omega' = \varepsilon R_\omega \tag{10}$$

where $R_\omega'$ is the spectral intensity of radiation emitted from a greybody. The engineering emissivity or absorptivity for diatomic and polyatomic gases is defined by a relation similar to Eq. (9). Thus, if $I_\omega$ is the spectrally emitted intensity from a non-black and a non-grey source, then the engineering emissivity E is given by

$$E = \int_0^\infty (I_\omega / \sigma T^4) \, d\omega \tag{11}$$

where $I_\omega$ is $R_\omega \left[1 - \exp(-P_\omega \, p\ell)\right]$, $P_\omega$ is the spectral absorption coefficient and $p\ell$ is the optical path density. Equation (11) can be written more explicitly as a sum over the contributions to the total emissivity from separate vibration- rotation bands. Thus, let

$\Delta\omega' = \Delta\omega (v_1, v_2^\ell, v_3 \rightarrow v_1', v_2^{\ell'}, v_3')$ represent the effective

width of the vibration-rotation band arising from the transition $v_1, v_2^{l}, v_3 \rightarrow v_1', v_2^{l'}, v_3'$. Then

$$\mathbb{B} = (\sigma T^4)^{-1} \sum_{v_1} \sum_{v_2} \sum_{l} \sum_{v_3} \sum_{v_1' \pm 1 v_1} \sum_{v_2' \pm 1 v_2} \sum_{l' \pm 1 l} \sum_{v_3' \pm 1 v_3} \int_{\Delta\omega'} R_\omega \left[ 1 - \exp\left(-P_\omega \, p l\right) \right] d\omega \qquad (13)$$

where the quantum numbers must conform to the selection rules for all allowed vibrational transitions. Quantitative calculations of $\mathbb{B}$ are exceedingly difficult to carry out.

## C. Total Absorptivity Determinations on Carbon Dioxide at Room Temperature

An apparatus has been built for the measurement of absorptivity and emissivity of carbon dioxide. The system consists of a source of infrared radiation, a gas cell in which temperature and pressure may be controlled and a non-selective receiver. The signal from the receiver or detector is amplified using chopped radiation for stabilization. The percentage of transmission is found by comparing voltage output from the detector for an empty cell with voltage output from the detector for the same cell under test conditions. A recording potentiometer (Speedomax) is used to indicate voltage. A block diagram of the apparatus used for study of absorption and emission is shown in Fig. 13.

The source of radiation used is a globar unit which has a continuous emission spectrum in the infrared region.

The globar temperature must be held within close limits to reduce fluctuations in radiation. Power supply to the globar is regulated by a Sola constant voltage transformer.

The globar, gas cell, and detecting thermocouple are placed in a wooden chamber which is flushed with nitrogen to prevent light absorption by atmospheric water and carbon dioxide. The cell is fitted with potassium chloride windows which allow transmission at wave lengths longer than 20 microns.

The detector is a thermocouple which develops a signal of 100 microvolts with full globar input. Sensitivity of the thermocouple is specified as six microvolts per microwatt of incident radiation. This thermocouple is of the same type as that used in the Perkin-Elmer Model 12C Spectrometer and is reported to be linear in output over wide variations in light intensity at all wavelengths in the near infrared region. The thermocouple is sensitive to ambient temperature changes. Drift and instability produced by such changes are avoided by chopping incoming radiation at 13 cycles per second. Thus a low frequency A.C. amplifier may be used to amplify the very low level signal from the thermocouple. The A.C. signal is later rectified and filtered to recover information regarding signal amplitude. Contacts for the synchronous rectifier are operated by means of cams on the shaft of the synchronous motor used for the rotating shutter.

Emissivity as well as absorptivity may be measured with this system. For emissivity measurements it is only necessary to place the light chopper disk between the sample and the thermocouple rather than between the globar and the gas sample.

Since percentage of transmission is measured by noting the difference in radiation intensity received when the cell is evacuated and the radiation received when the cell contains gas at known temperature and pressure, it is important that measurements be made within the limits of linearity of the detecting and amplifying system. There is no easy means available for the measurement of absolute radiation intensity received at the thermocouple. The amplifier and Speedomax were found to be linear with respect to input signals from the detector.

Percentage of absorption by carbon dioxide at the temperature and pressure used was found to be of the order of 25% or less. In order to get reliable data it is necessary that noise and drift be low in comparison with variations in signal strength arising from changes in absorption of radiation. Noise and drift in the instrument were reduced to below the 1% level.

Previous investigations[10] were carried out at a total pressure of one atmosphere while varying the partial pressure of the absorbing or radiating gas. We have investigated absorption of radiation at room temperature at total pressures up to 55 atmospheres.

Let D = recorder deflection for the filled gas cell and $D_1$ = the deflection for the empty cell, K = recorder constant, $T_s$ = globar temperature, $\varepsilon_s$ = emissivity of source, $\sigma$ = Stephan-Boltzmann constant, $\alpha$ = absorptivity and $K' = K/\sigma$. Then

$$KD_1 = \sigma \varepsilon_s T_{sl}^4 \tag{14}$$

and, if $\varepsilon_s = 1$,

$$K' = T_{sl}^4/D_1 \tag{15}$$

When the gas cell contains absorbing gas and $\varepsilon_s = 1$, then

$$K'D = (1-\alpha)T_{sl}^4 \tag{16}$$

$$\alpha = (T_{sl}^4 - K'D)/T_{sl}^4 \tag{17}$$

$$\alpha = 1 - D/D_1 \tag{18}$$

It follows from Kirchoff's law that the total absorptivity and emissivity of the carbon dioxide are equal to each other at equilibrium. At room temperature it has been assumed that the emission of radiation from carbon dioxide is negligibly small compared with the intensity of the transmitted incident radiation. The results of total absorption measurements are presented in Tables III and IV and are plotted in Figs. 14 to 17. Table III and Fig. 14 contain a summary of the experimental data which were actually

obtained. Table IV and Figs. 15 and 16 contain results applicable to a total pressure of 1 atmosphere. In Fig. 17 the absorptivity is plotted as a function of optical density with the total pressure $p_T$ treated as a variable parameter. Reference to Fig. 17 shows that $\alpha$ is not a sensitive function of the total pressure at pressures in excess of about 3.73 atm.

Table IV. Absorptivity of Carbon Dioxide at a Pressure of 1 atm and at Room Temperature

| $p\ell$ (ft-atm) | Absorptivity $\alpha$ | $p\ell$ (ft-atm) | Absorptivity $\alpha$ |
|---|---|---|---|
| 10 | .221 | .4 | .081 |
| 8 | .197 | .3 | .064 |
| 6 | .172 | .1 | .054 |
| 4 | .148 | .08 | .050 |
| 3 | .122 | .06 | .045 |
| 1.5 | .113 | .04 | .039 |
| 1.0 | .103 | .02 | .030 |
| .8 | .098 | .01 | .022 |
| .6 | .092 | | |

D. Comparison with the Results of Other Investigators

The experimentally determined values of $\alpha$ at a total pressure of 1 atm are compared with the results of studies carried out by Hottel and Mangelsdorf[11] in Table V and in Figs. 18 and 19.

Since the limit of our probable error is ± 10% and those of Hottel and Mangelsdorf ± 20%, the agreement between the independently determined experimental data may be considered to be satisfactory.

Table V. Absorptivity of Carbon Dioxide at Room Temperature at a Total Pressure of 1 Atmosphere.

| $p\ell$ (ft atm) | Absorptivity $\alpha$ Hottel and Mangelsdorf (1935) | Present Study |
|---|---|---|
| 10 | | .221 |
| 8 | | .197 |
| 6 | | .172 |
| 4 | .17 | .148 |
| 2 | .15 | .122 |
| 1.5 | .14 | .113 |
| 1.0 | .128 | .103 |
| .8 | .120 | .098 |
| .6 | .111 | .092 |
| .4 | .100 | .081 |
| .2 | .083 | .067 |
| .1 | .068 | .054 |
| .08 | .064 | .050 |
| .06 | .057 | .045 |
| .04 | .050 | .039 |
| .02 | .038 | .030 |
| .01 | .0285 | .022 |
| .008 | .0252 | |
| .006 | .0219 | |
| .004 | .017 | |

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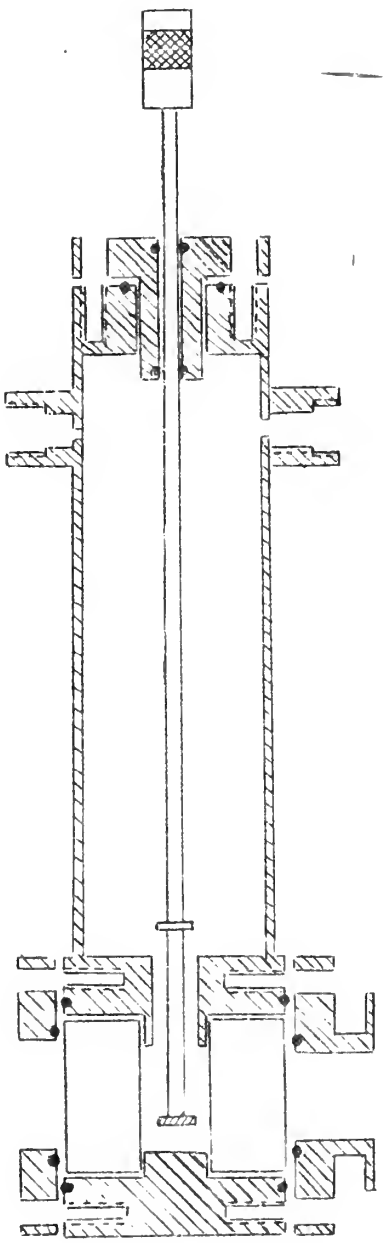
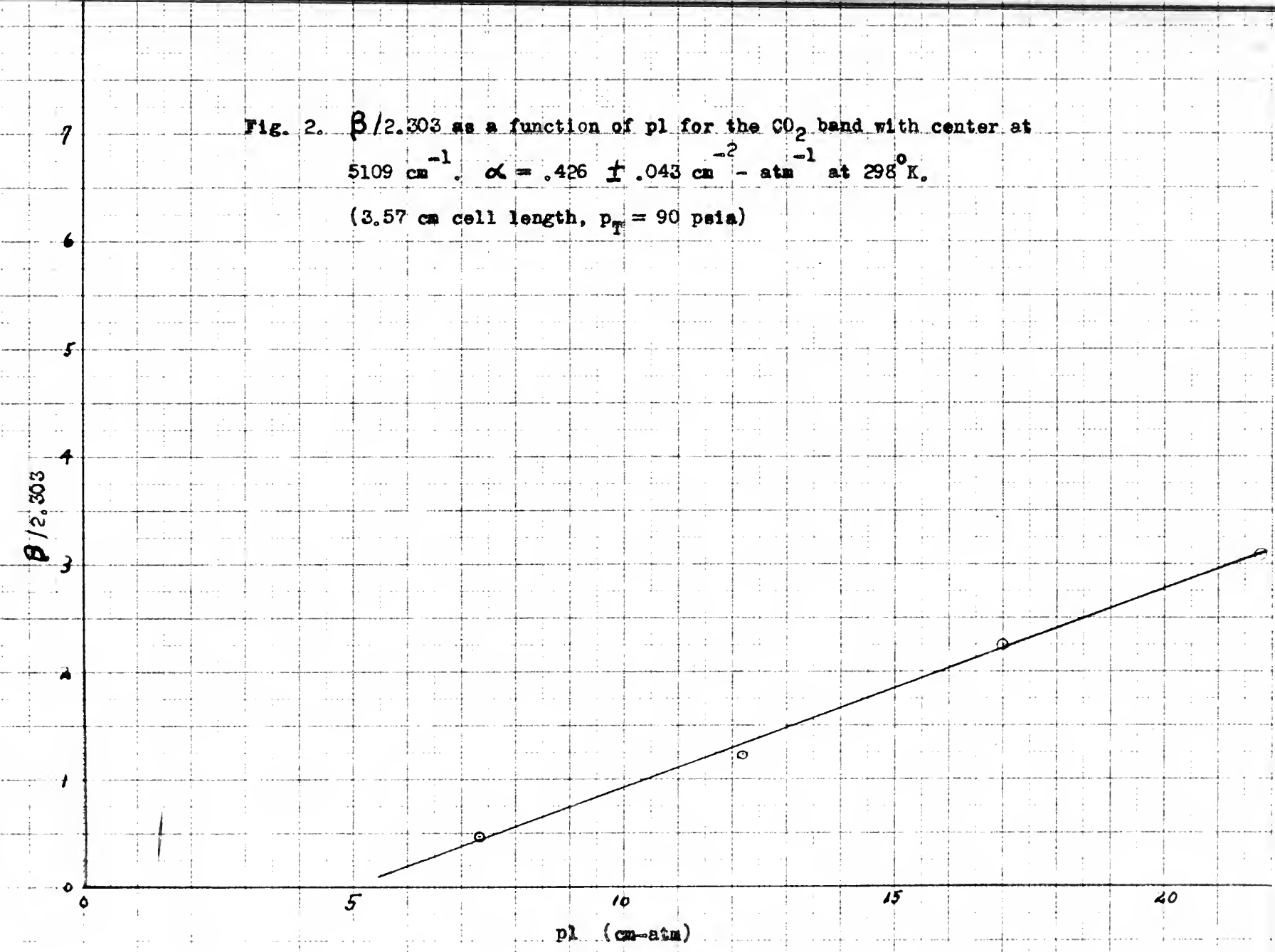


Fig. 1. Schematic representation of infrared absorption cell used to measure intensities of gas mixtures.

Fig. 2. $\beta/2.303$ as a function of pl for the $CO_2$ band with center at 5109 $cm^{-1}$. $\alpha = .426 \pm .043$ $cm^{-2} - atm^{-1}$ at 298°K.
(3.57 cm cell length, $p_T$ = 90 psia)



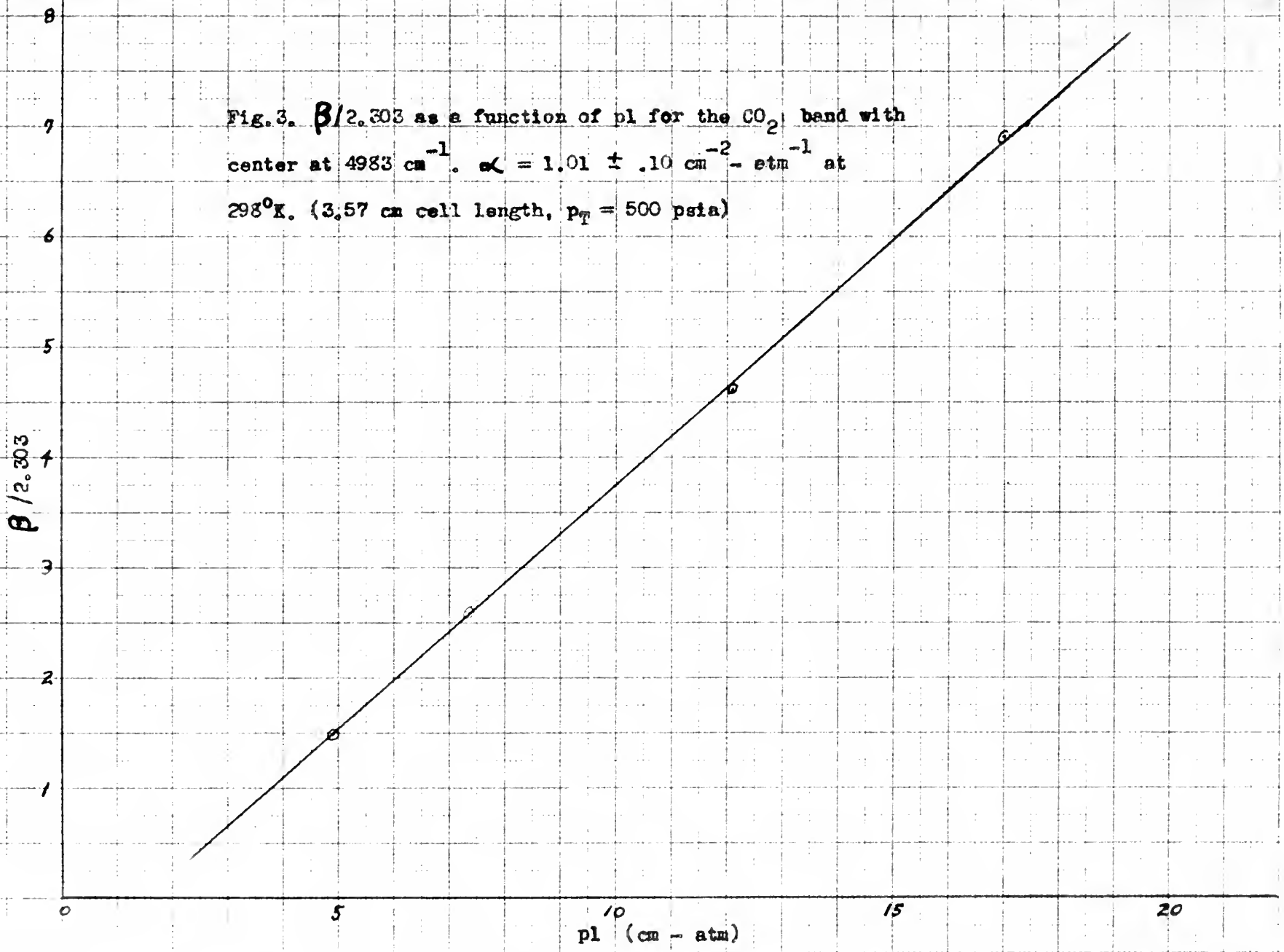
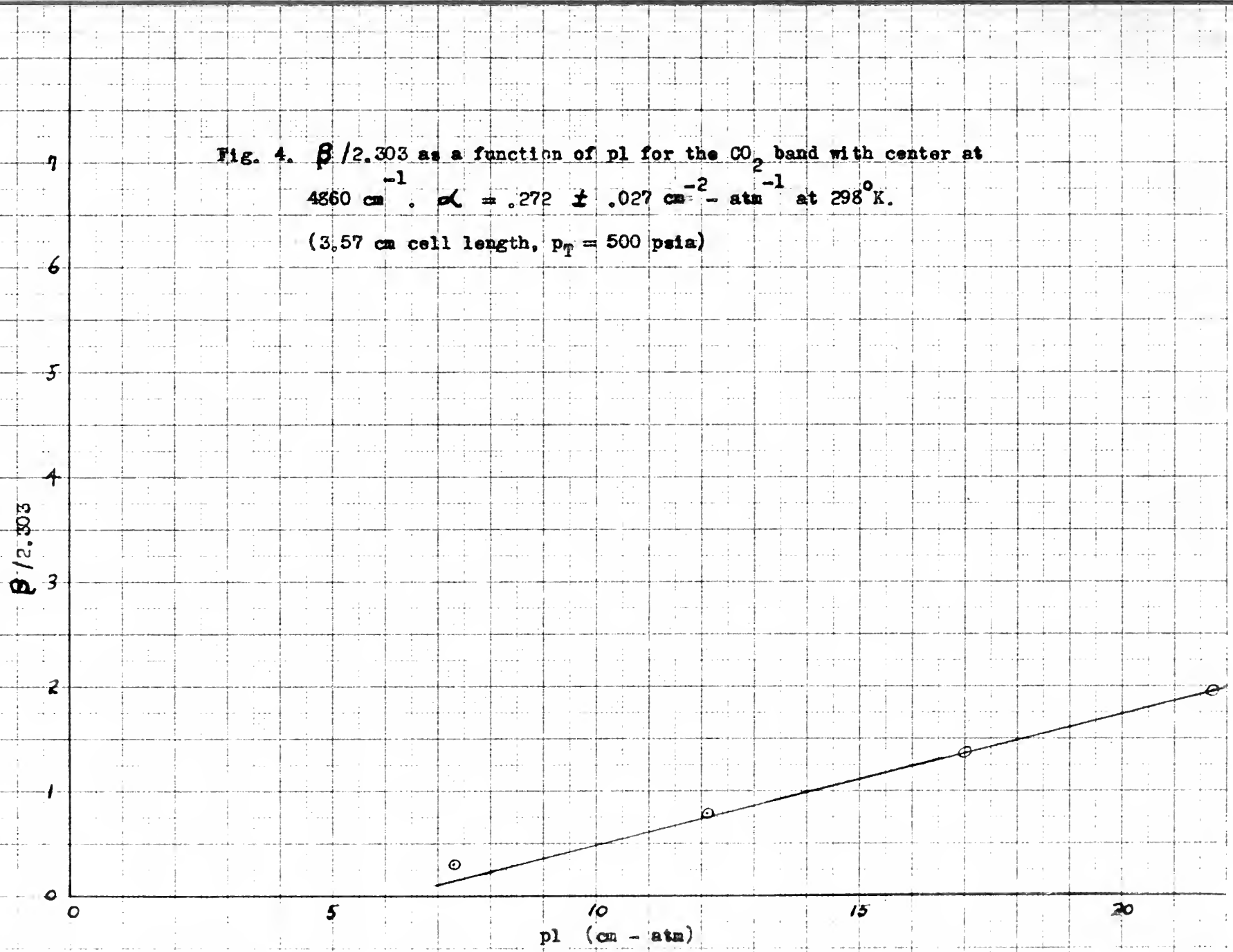



Fig. 3. $\beta/2.303$ as a function of pl for the $CO_2$ band with center at 4983 $cm^{-1}$. $\alpha = 1.01 \pm .10$ $cm^{-2} - atm^{-1}$ at 298°K. (3.57 cm cell length, $p_T$ = 500 psia)

Fig. 4. $\beta/2.303$ as a function of pl for the $CO_2$ band with center at 4860 $cm^{-1}$. $\alpha$ = .272 ± .027 $cm^{-2}$ - $atm^{-1}$ at 298°K.

(3.57 cm cell length, $p_T$ = 500 psia)



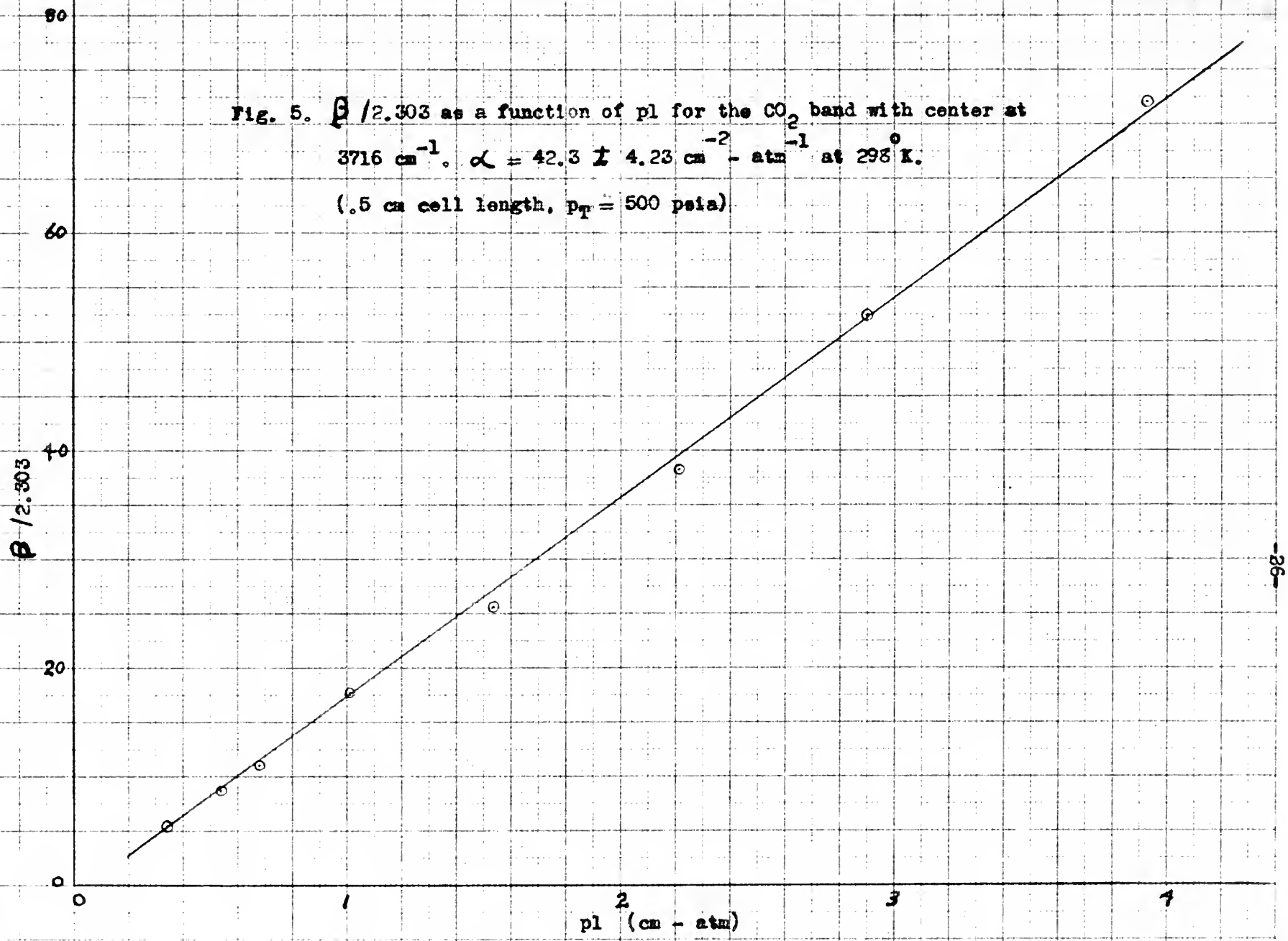



Fig. 5. $\beta$ /2.303 as a function of pl for the $CO_2$ band with center at 3716 $cm^{-1}$. $\alpha$ = 42.3 ± 4.23 $cm^{-2}$ - $atm^{-1}$ at 298° K.
(.5 cm cell length, $p_T$ = 500 psia)

Fig. 6. $\beta/2.303$ as a function of pl for the $CO_2$ band with center at 4609 $cm^{-1}$. $\alpha = 28.50 \pm 2.85$ $cm^{-2}$ - $atm^{-1}$ at 298°K.
(.5 cm cell length, $p_T$ = 500 psia)

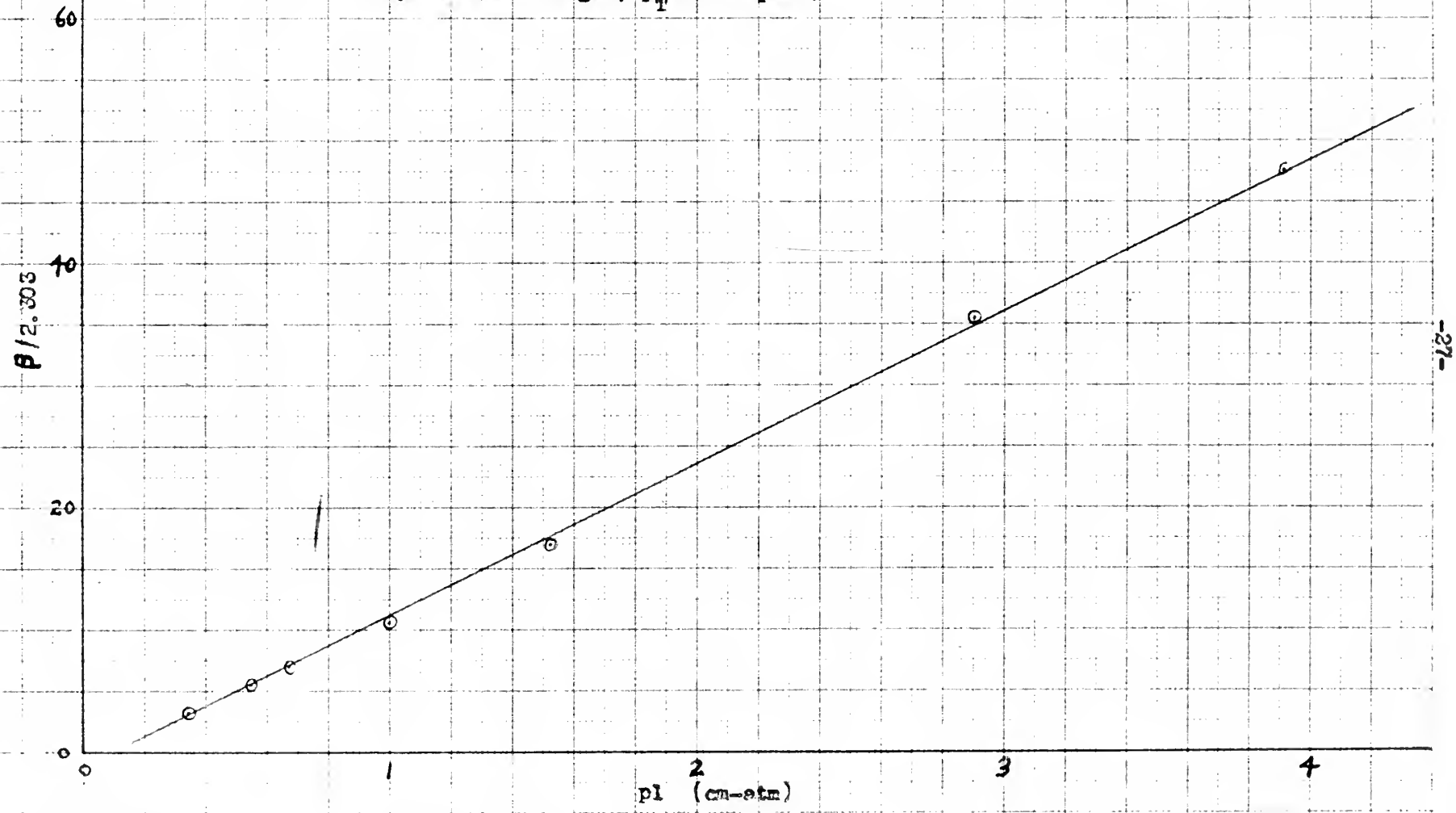


Fig. 7. $\beta / 2303$ as a function of pl for the $CO_2$ band with center at 2349 $cm^{-1}$. $\alpha = 2706 \pm 270$ $cm^{-2} - atm^{-1}$ at 298°K.

(5.15 cm cell length, $p_T = 700$ psia)

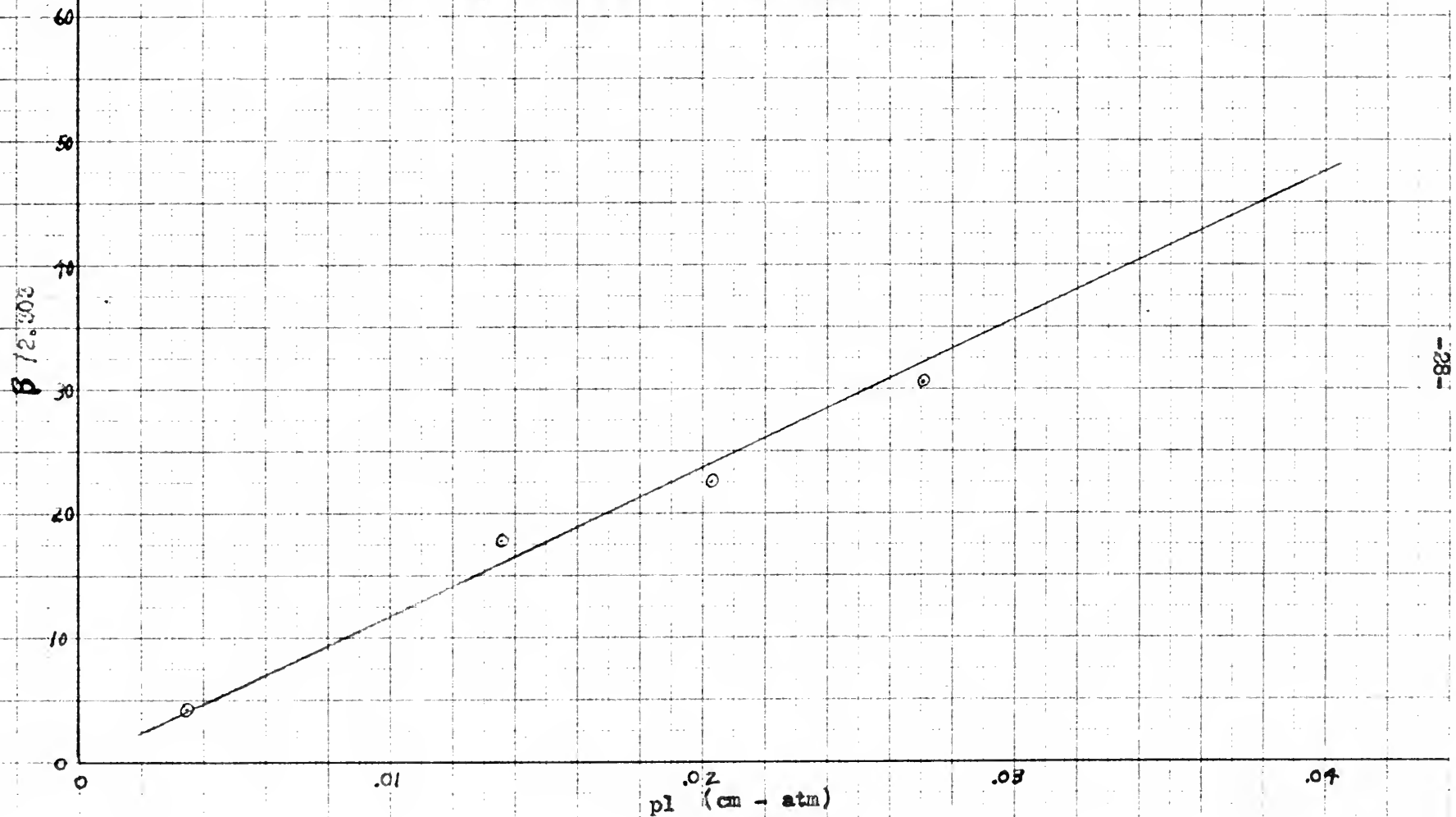


Fig. 8. $\beta / 2.303$ as a function of pl for $CO_2$ in the region between 2000 and 2160 $cm^{-1}$. $\alpha = .147 \pm .047$ $cm^{-2} - atm^{-1}$ at $298^{\circ}K$. (3.57 and 6.72 cm cell length, $p_T = 500$ psia)

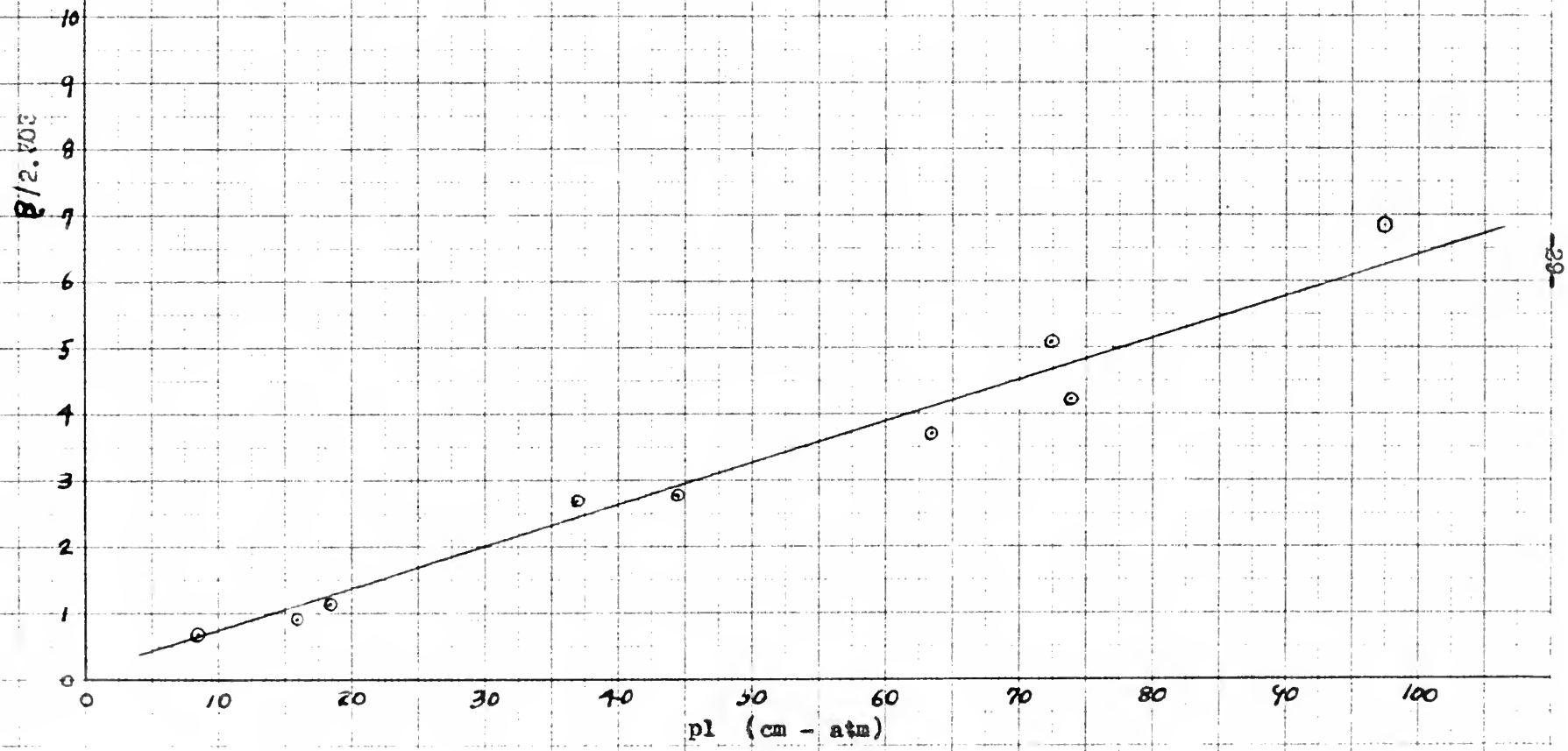


Fig. 9. $\beta/2.303$ as a function of pl for $CO_2$ in the region between 1800 and 2000 $cm^{-1}$. $\alpha$ = .083 ± .008 $cm^{-2}$ - $atm^{-1}$ at 298°K. (6.72 cm cell length, $p_T$ = 400 psia)

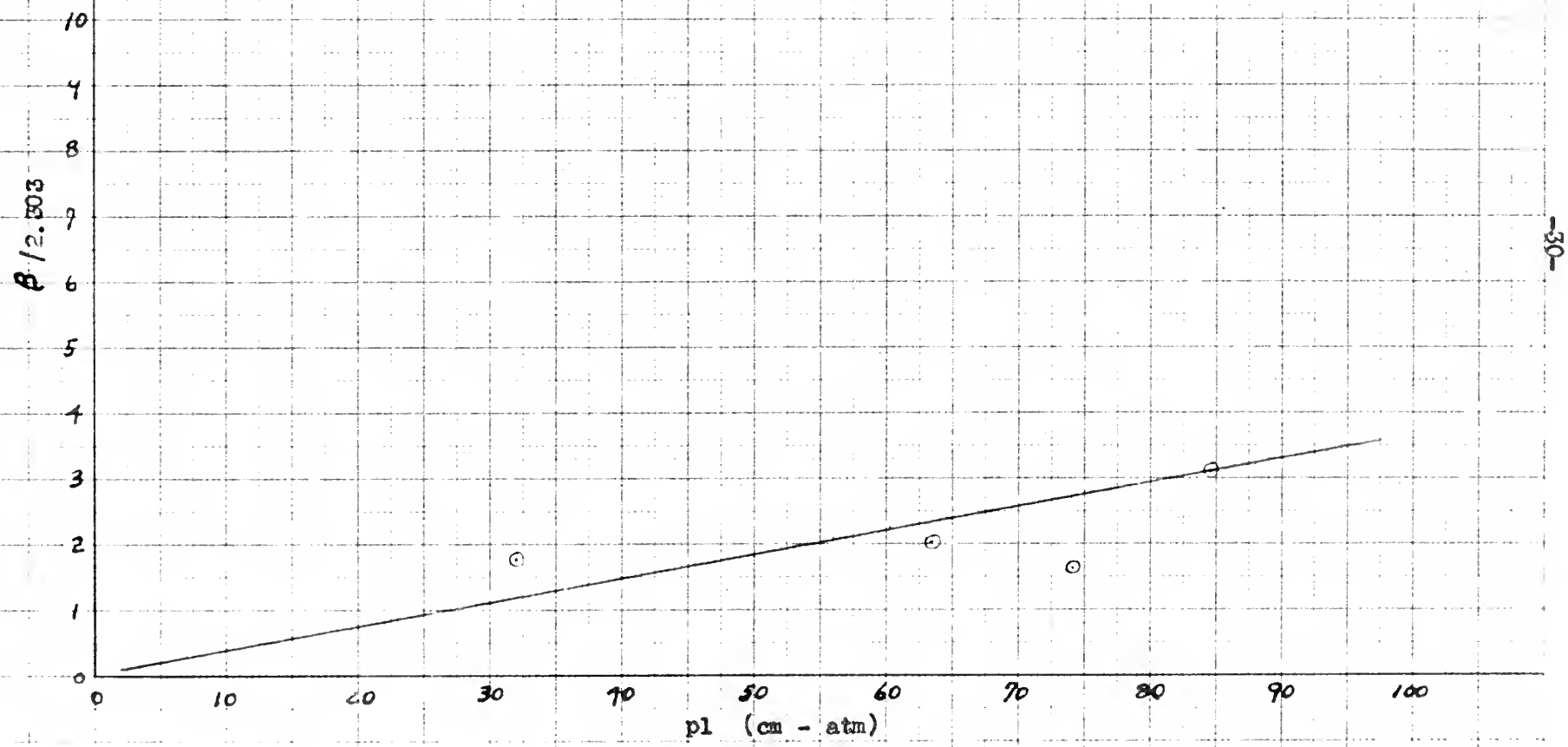
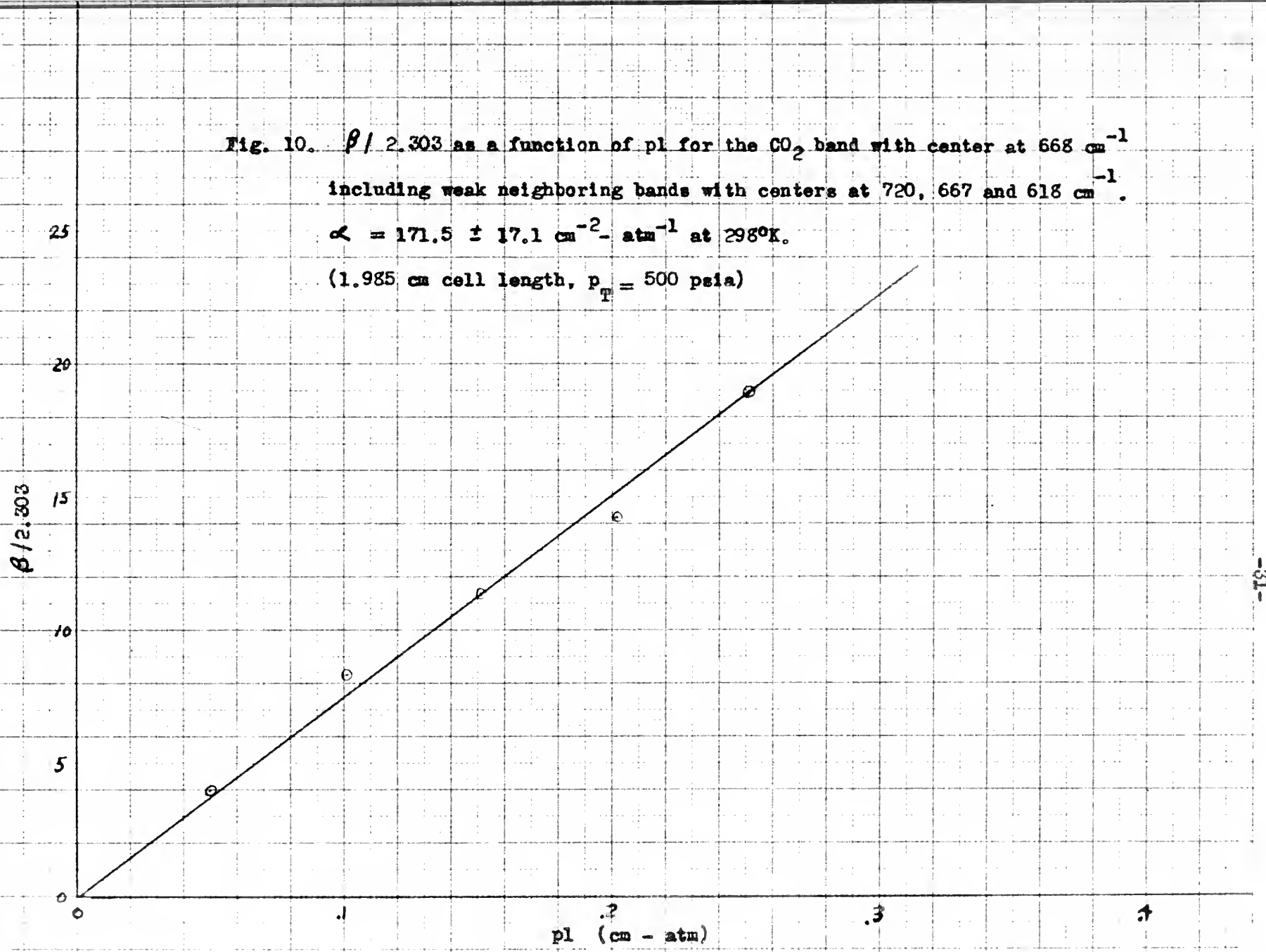


Fig. 10. $\beta / 2.303$ as a function of pl for the $CO_2$ band with center at 668 $cm^{-1}$ including weak neighboring bands with centers at 720, 667 and 618 $cm^{-1}$.

$\alpha = 171.5 \pm 17.1\ cm^{-2} \cdot atm^{-1}$ at 298°K.

(1.985 cm cell length, $p_T = 500$ psia)



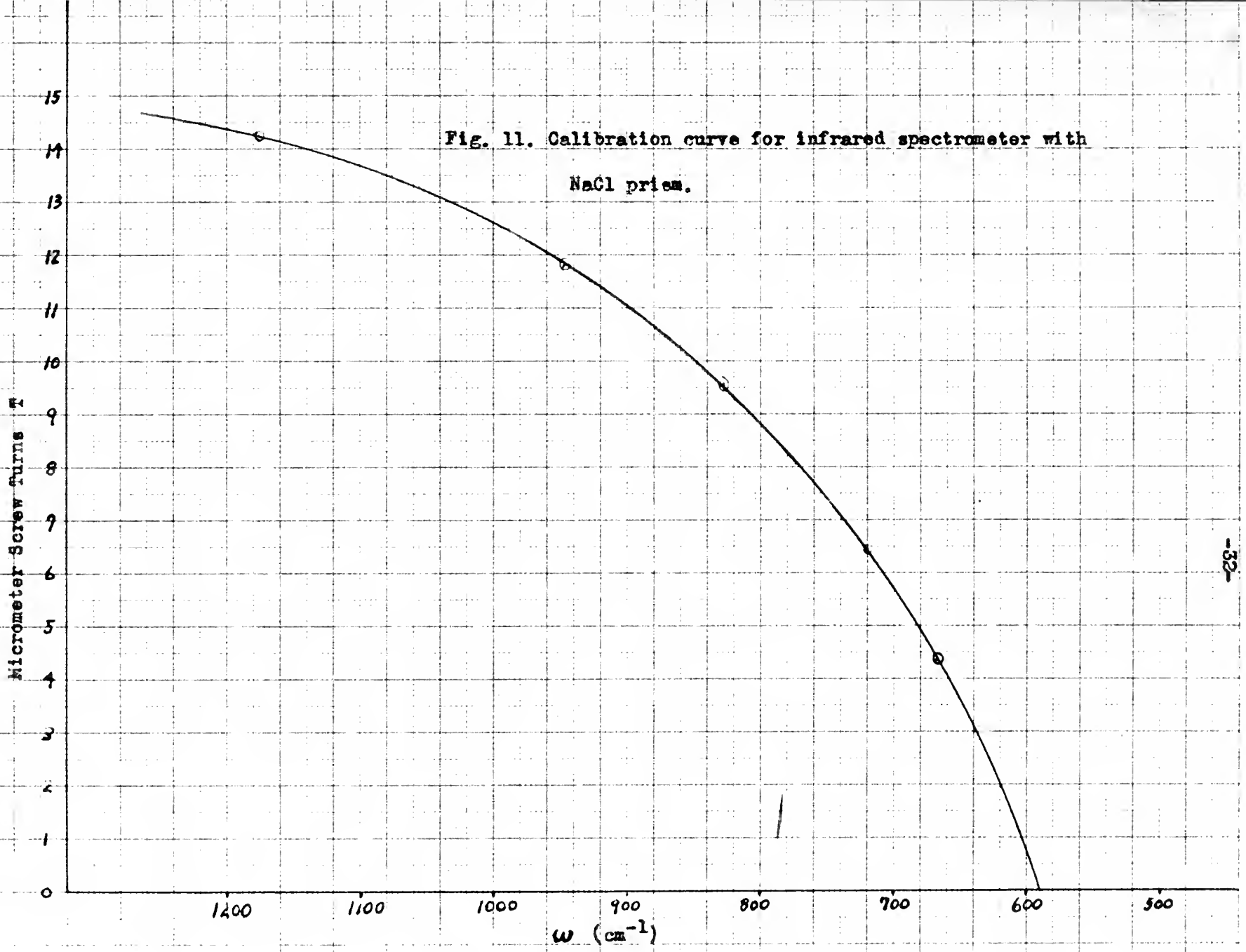



Fig. 11. Calibration curve for infrared spectrometer with NaCl prism.

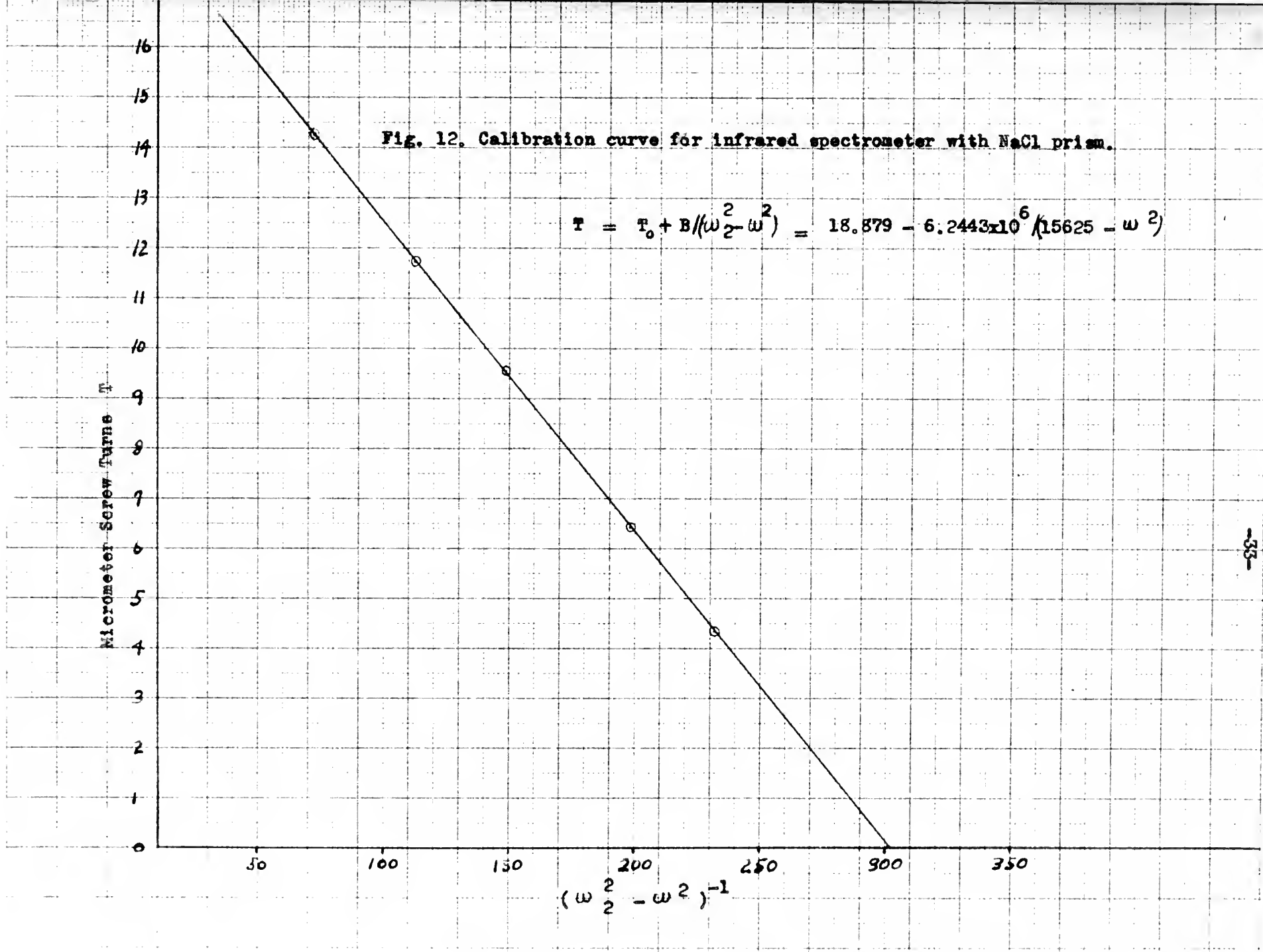



Fig. 12. Calibration curve for infrared spectrometer with NaCl prism.

$$T = T_0 + B/(\omega_2^2 - \omega^2) = 18.879 - 6.2443 \times 10^6/(15625 - \omega^2)$$

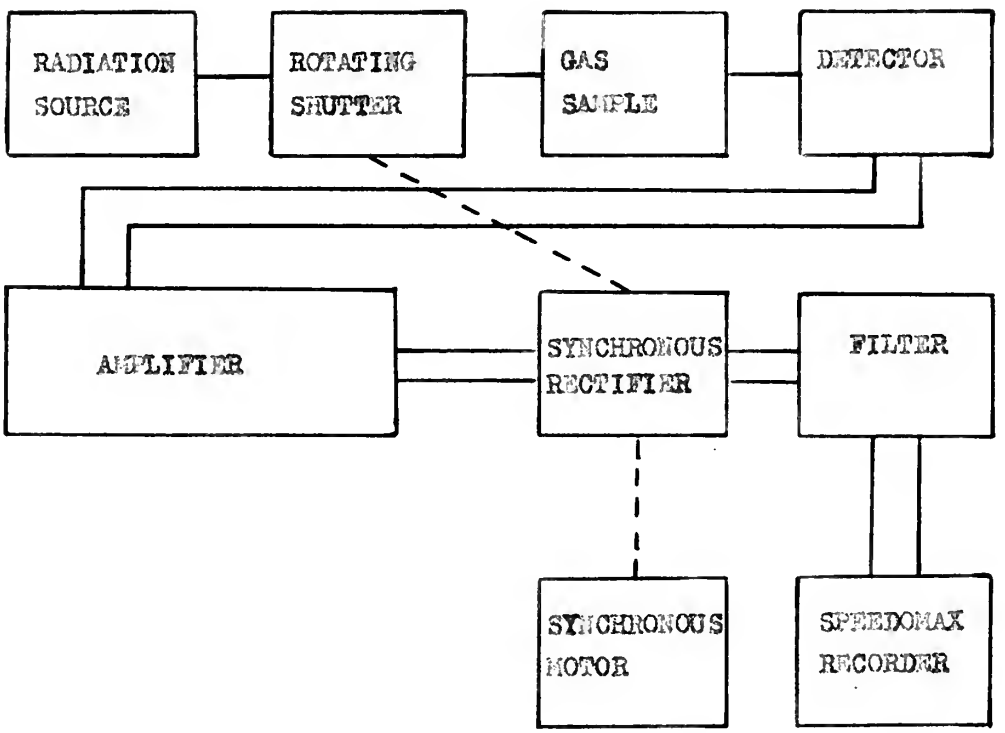



Figure 13. Block diagram of apparatus for measurement of total absorption of infrared radiation.

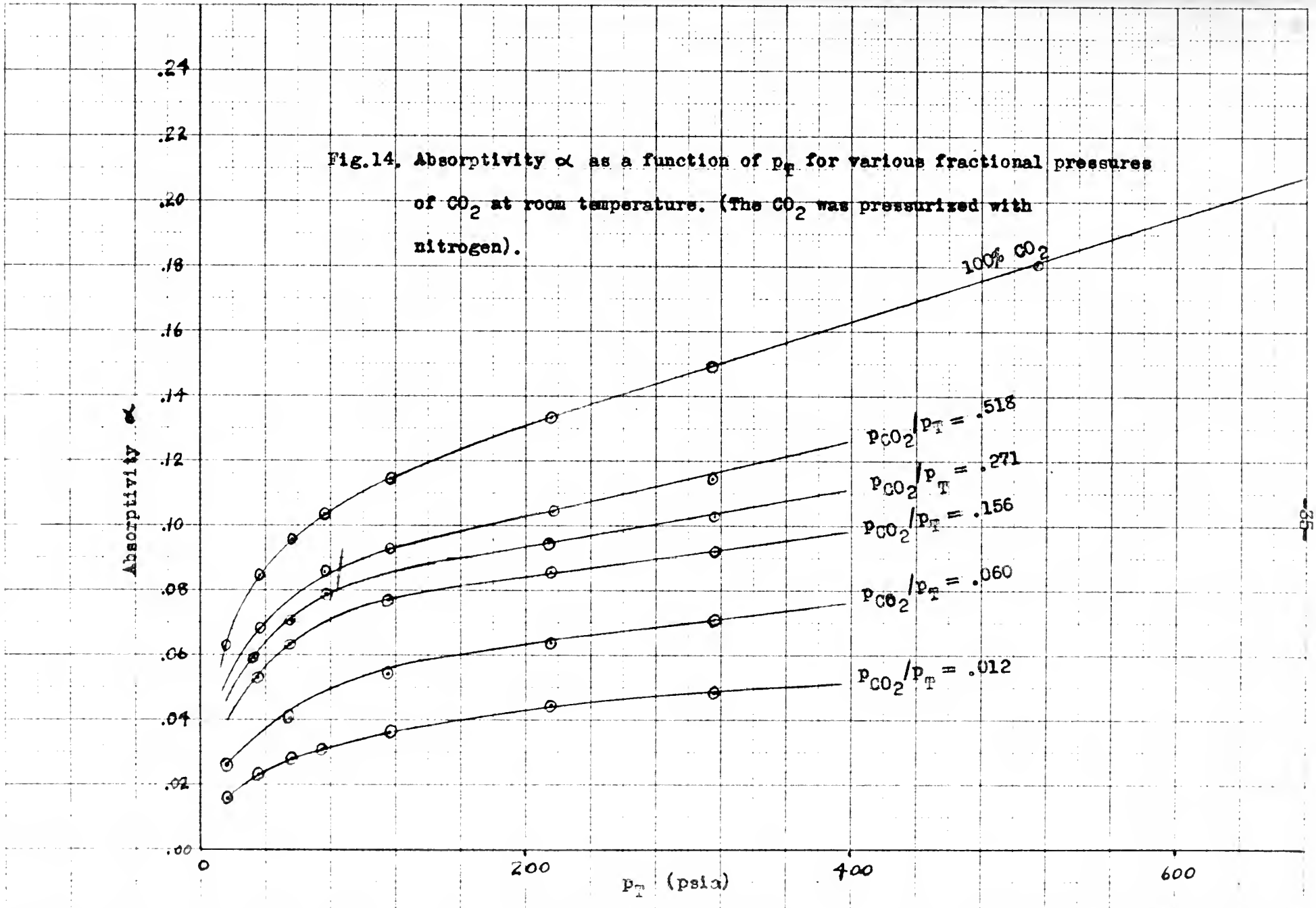
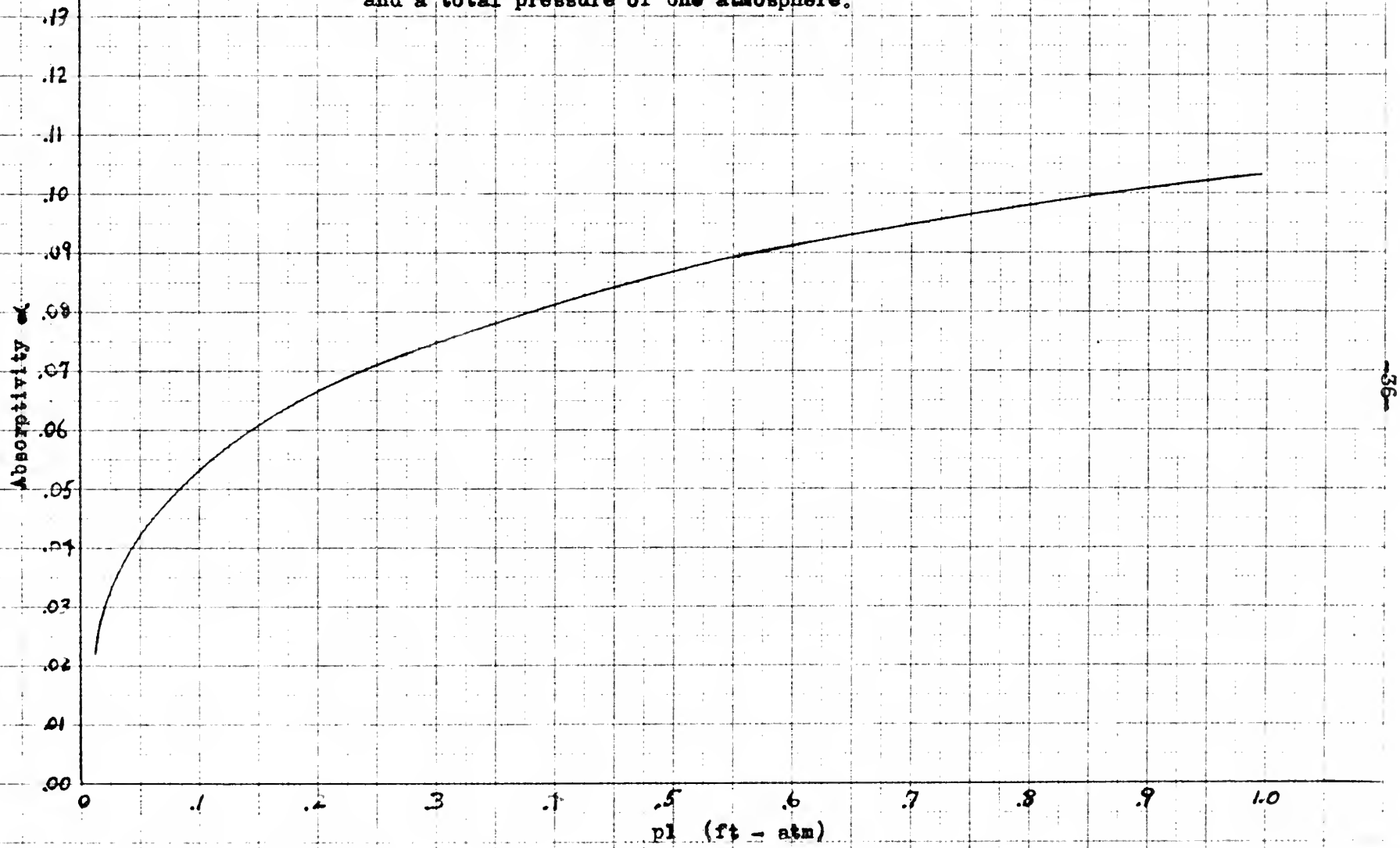



Fig.14. Absorptivity ∝ as a function of $p_T$ for various fractional pressures of $CO_2$ at room temperature. (The $CO_2$ was pressurized with nitrogen).

Fig. 15. Absorptivity $\alpha$ as a function of pl for $CO_2$ at room temperature and a total pressure of one atmosphere.



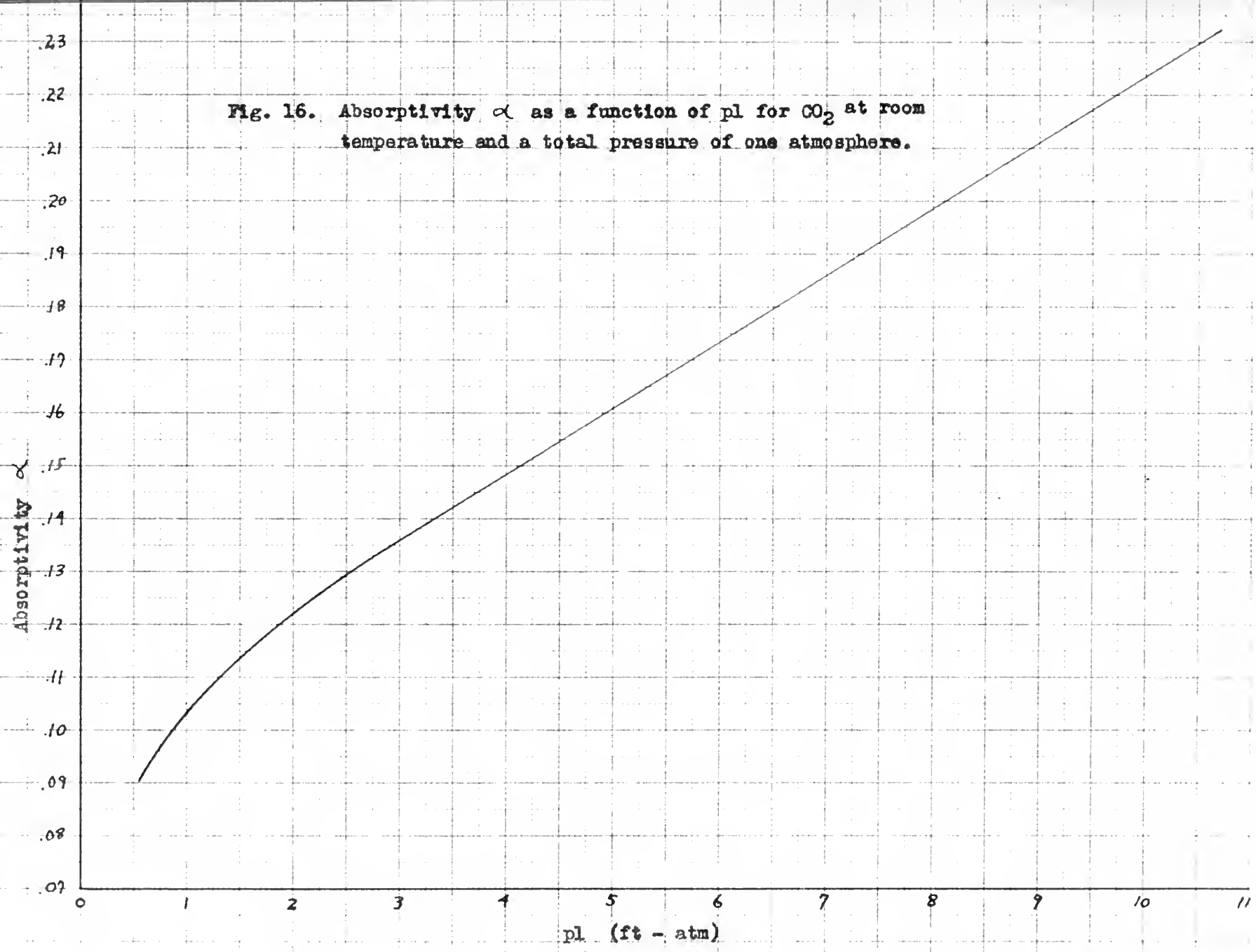



Fig. 16. Absorptivity $\alpha$ as a function of pl for $CO_2$ at room temperature and a total pressure of one atmosphere.

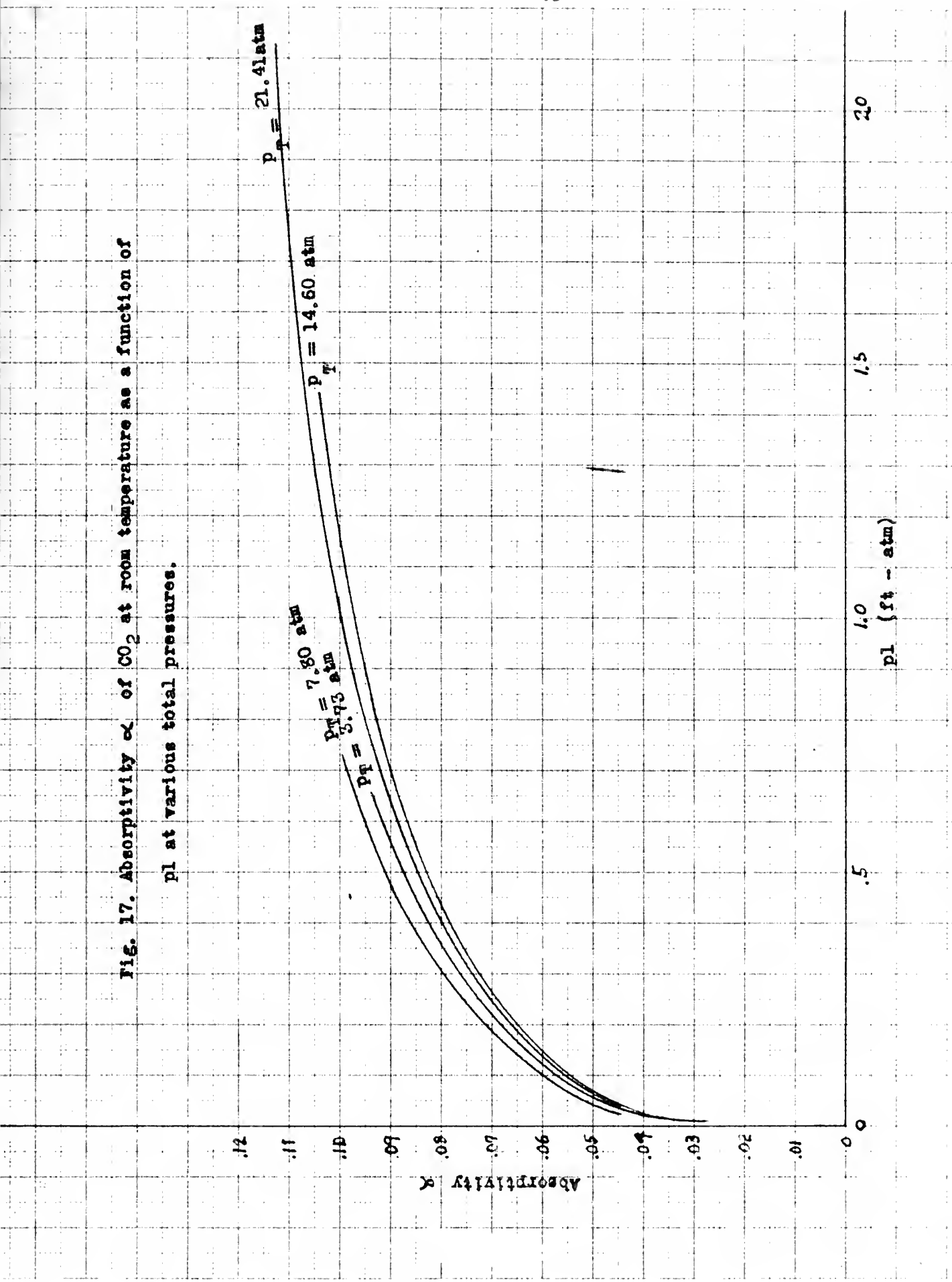



Fig. 17. Absorptivity $\alpha$ of $CO_2$ at room temperature as a function of pl at various total pressures.

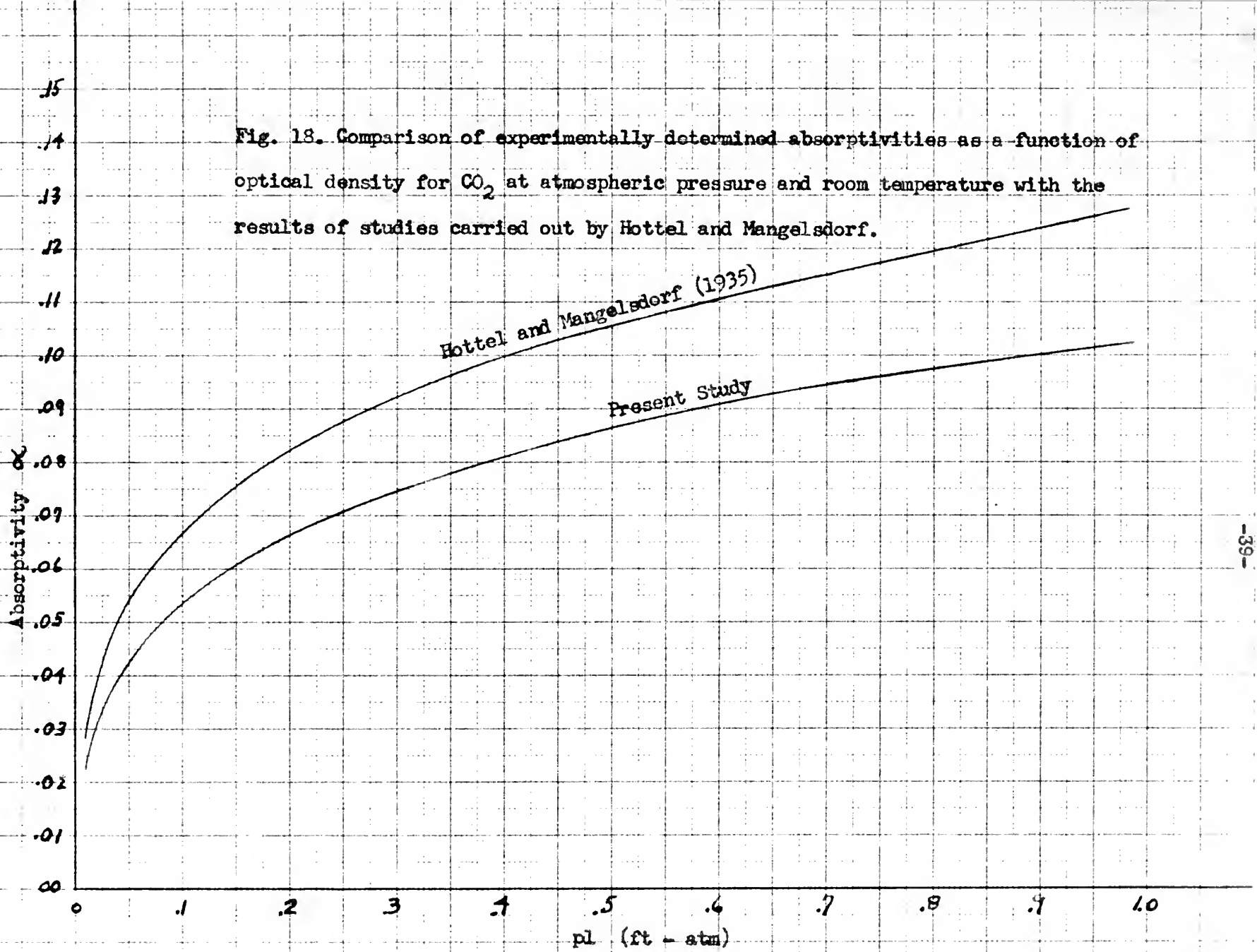



Fig. 18. Comparison of experimentally determined absorptivities as a function of optical density for $CO_2$ at atmospheric pressure and room temperature with the results of studies carried out by Hottel and Mangelsdorf.

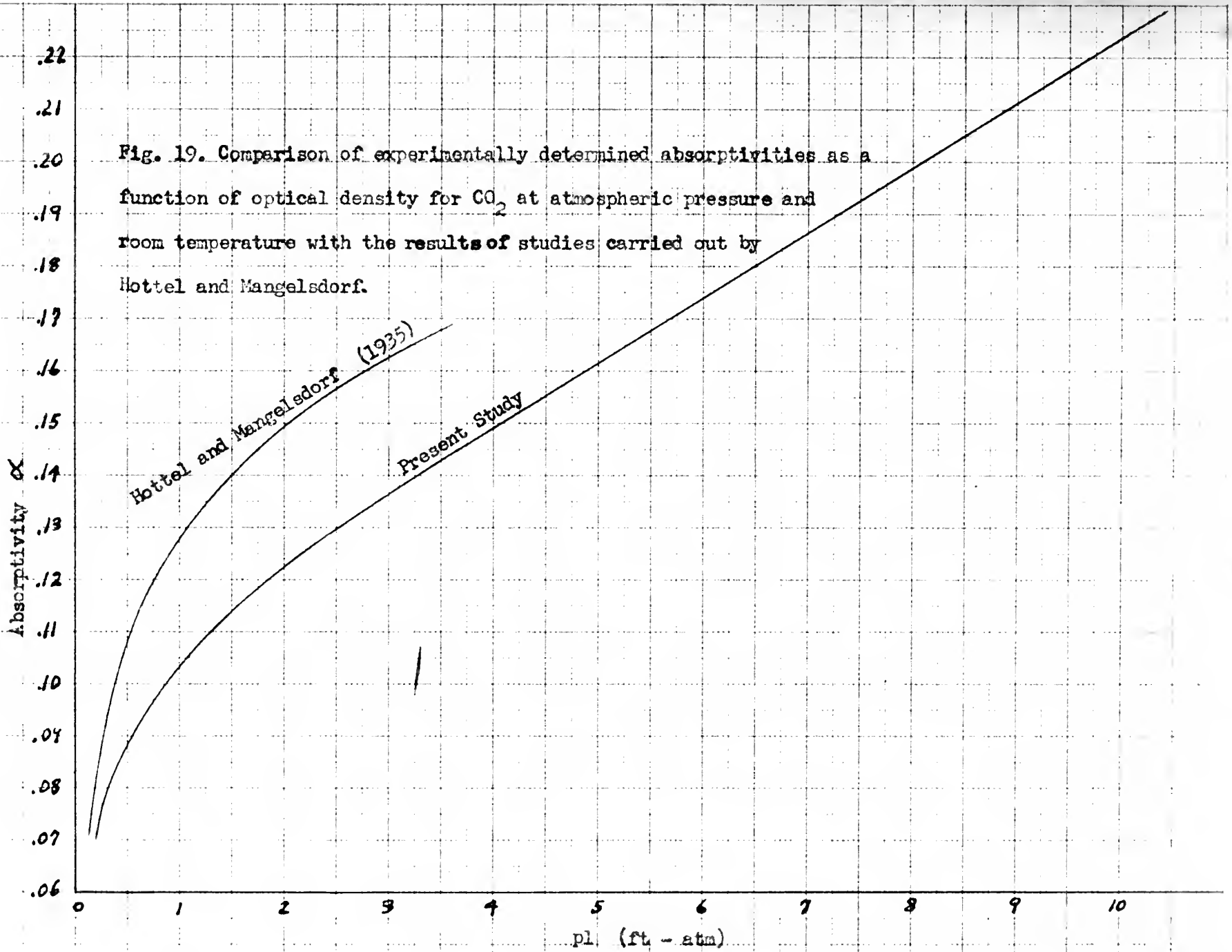



Fig. 19. Comparison of experimentally determined absorptivities as a function of optical density for $CO_2$ at atmospheric pressure and room temperature with the results of studies carried out by Hottel and Mangelsdorf.